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Recovery of Zircon From Investment Casting Molds

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb/ton	pound per ton
gal	gallon	min	minute
h	hour	μm	micrometer
in	inch	pct	percent
L	liter		

RECOVERY OF ZIRCON FROM INVESTMENT CASTING MOLDS

By C. W. Smith[1] and T. O. Llewellyn[2]

ABSTRACT

The Bureau of Mines conducted physical and chemical beneficiation studies on three samples of waste investment casting molds to devise a method to liberate and recover zircon. Rod mill grinding, autogenous attrition grinding, and caustic leaching were liberation methods investigated. Flotation, gravity separation, and caustic leaching and sizing were recovery methods investigated. Flotation techniques produced concentrates containing up to 74.2 pct zircon with a zircon recovery of 53.4 pct. Gravity concentration produced concentrates containing up to 98.6 pct zircon; however, recovery of the zircon was only 57 pct. Caustic leaching and sizing produced concentrates containing up to 98 pct zircon with attendant recoveries of 81 pct.

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INTRODUCTION

Investment casting presents a number of advantages over more conventional casting methods. Almost any shape, simple or complex, can be investment cast. Holes, slots, bevels, serrations, thin sections, knife edges, screw threads, and other configurations can be directly cast by investment casting. Close dimensional tolerances are possible and many parts can be used "as cast" with no additional machining. Manufacturing capacity can be increased as machine tools for milling, turning, and boring are required for only minor finish machining operations. Finally, practically any alloy may be investment cast (1-2).[3]

Investment casting or the "lost wax" process dates back in time to the Shang Dynasty in China (1766-1122 B.C.) (2). Modern techniques for the production of investment casting molds follow several basic steps. The process begins with the manufacture of a heat-disposable pattern which is made by injecting wax or plastic into a metal die. The patterns are then assembled into a cluster by attaching the gate of each pattern to a heat disposable runner. The entire cluster is then dipped into a ceramic slurry, drained, and coated with fine ceramic sand (zircon). This process is repeated several times. Then the cluster is backed with several coats of coarser ceramic materials such as mullite, alumina, or fused silica until a self-supporting shell from 1/2-in to 5/8-in thick is formed. Figure 1 is a cross section of one of the mold samples showing the layered structure resulting from the repetition of the dipping and coating steps. The coated cluster is then placed in a high-temperature furnace where the wax pattern melts and is removed through the gates and runners (1-2).

Zircon exhibits several properties making it an ideal material for the manufacture of casting molds, among which are its refractoriness, low expansion, reduced wettability by molten metals, high thermal conductivity, and high heat capacity. Low expansion gives improved stability of the molds at high temperatures. Reduced wettability and refractoriness result in improved surface finish and reduced mold penetration. High thermal conductivity and high heat capacity result in improved control of metal solidification (3-5).

The Steel Founders Society of America has designated a standard specification for zircon sand and zircon flour. This standard specifies a minimum of 97 pct zircon. Maximum limits of titania, iron, and free silica, are 0.35, 0.40, and 1.0 pct, respectively (6).

Average prices for zircon sand and flour in 1983 were $165 and $225 per ton, respectively. Imports of zircon for the same year were 30 pct of a total consumption of 120,000 short tons. Approximately 49 pct of this zircon was used in foundry applications (7). Due to the high cost of materials used in the manufacture of the molds, investment casting is principally used in the production of low volume, high cost articles such as jet turbine blades. Development of methods to recover the expensive zircon used in the molds could make investment casting a feasible method for use on high-volume, low-cost articles. For this reason, as well as conserving domestic resources and reducing dependence on foreign supplies, the Bureau of Mines conducted research to devise technology for recovering zircon from waste investment casting molds.

DESCRIPTION OF SAMPLES

Three 55-gal drum samples of waste investment casting molds were obtained for this study, two from turbine manufacturers and the other from a steel foundry. Zircon composed 22 to 60 pct of the material in the molds. Other constituents in the molds were mullite, alumina, quartz, cristobalite, and fused silica. Figure 2 is a photograph of the mold samples as received. A description of each of the samples follows.

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

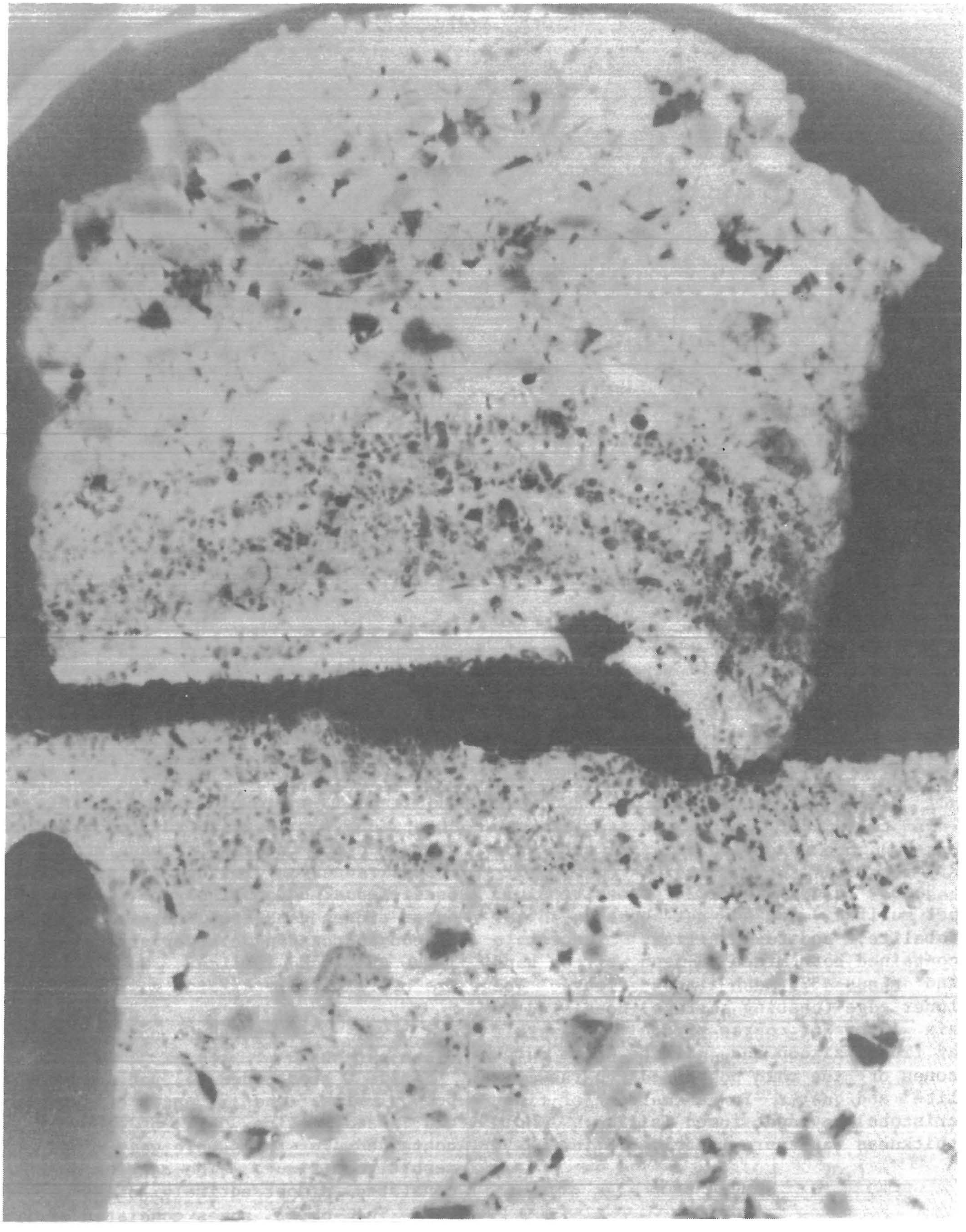

FIGURE 1. - Magnified cross section of typical mold sample showing layered structure.

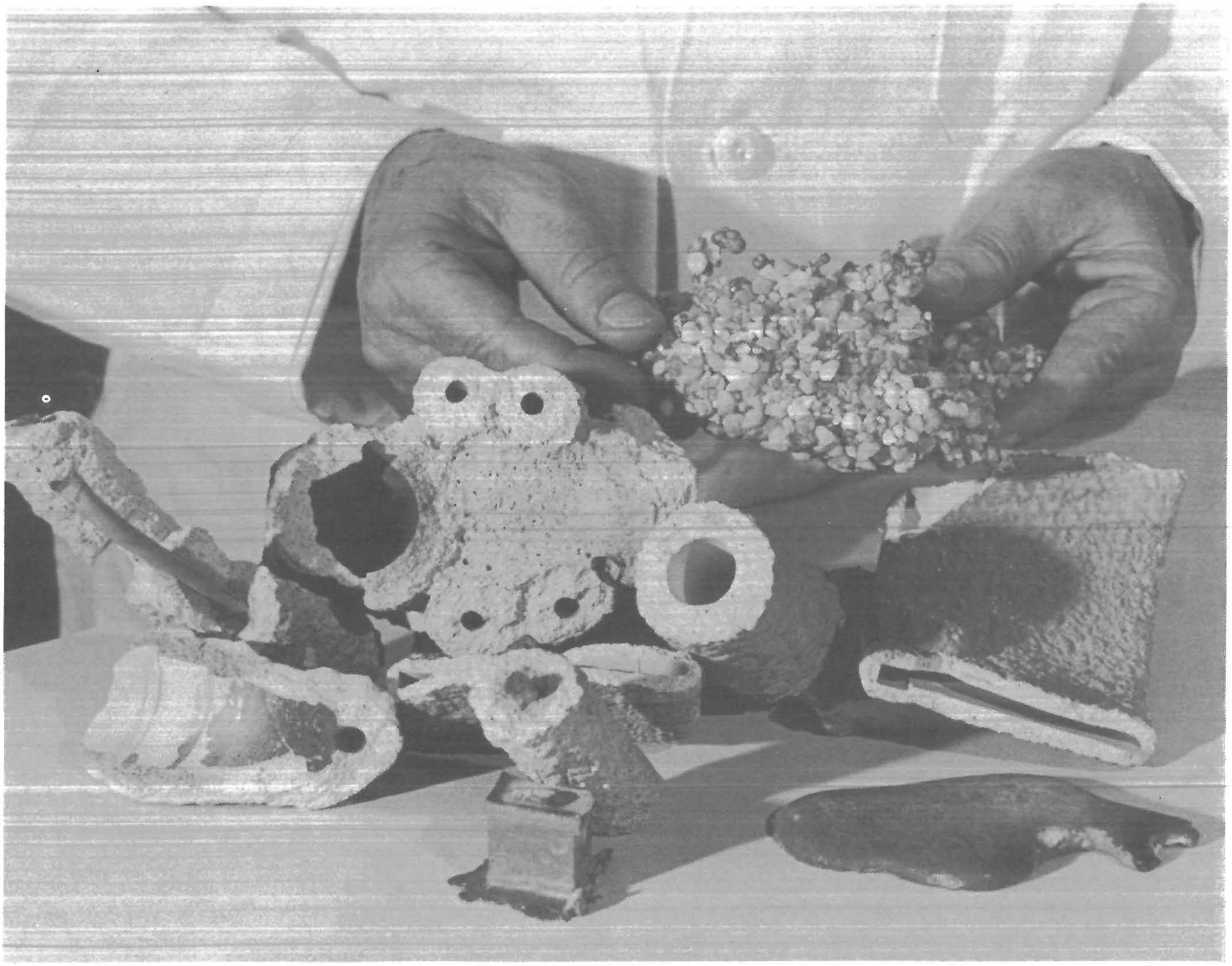

FIGURE 2. - Photograph of mold samples as received.

SAMPLE A

Sample A contained 22 pct zircon, 33 pct mullite, and 44 pct quartz, cristobalite, and fused silica. The sample contained both minus 65-mesh zircon sand and minus 325-mesh zircon flour. The inner edge (casting surface) consisted of six layers of coarse zircon in a matrix of finer zircon and mullite. The outer zones of the mold contained coarse mullite and quartz in a matrix of finer cristobalite and fused silica. Mold thickness was approximately 5/8 in.

SAMPLE B

Sample B contained 60 pct zircon, 21 pct mullite, and 18 pct quartz, cristobalite, and fused silica. All zircon contained in the sample was minus 325-mesh zircon flour. The casting surface consisted almost entirely of zircon. The outer zones consisted of fine grained zircon surrounding coarser grains of mullite and fused silica. Mold thickness was approximately 1/2 in.

SAMPLE C

Sample C contained 44 pct zircon, 48 pct alumina, and 7 pct cristobalite and fused silica. All of the zircon contained in the sample was minus 325-mesh zircon flour. The casting surface consisted almost entirely of fine zircon. The outer zones consisted of fine zircon surrounding coarse grains of alumina. Mold thickness was approximately 1/2 in.

LIBERATION STUDIES

Two types of binders, colloidal silica and ethyl silicate, are used in mold manufacture. Upon firing, each of these binders produces silica bonds between the individual grains (1-2). Destruction of these silica bonds is necessary for complete liberation of the mold constituents. Three methods of liberation were investigated: conventional rod-mill grinding, attrition grinding, and caustic leaching. Prior to testing each method of liberation, samples were crushed to pass 20 mesh. Results on sample A are discussed to illustrate the relative effectiveness of each liberation method.

Rod-mill grinding was unsatisfactory as a method of liberation. Large amounts of silica binder were left adhering to the zircon grains, causing the zircon grains to behave like silica and reducing the selectivity of subsequent beneficiation. As a result, grade and recovery of concentrates were reduced. Figure 3*A* is a magnified photograph of minus 200-mesh zircon grains showing the adherence of the silica binder.

Autogenous attrition grinding was investigated using the Bureau-devised turbomill (8). Samples were ground for 10 and 20 min in the 5-in mill. Turbomilling, which grinds by attrition, resulted in cleaner surfaces on the zircon grains but also generated excessive fine zircon that was lost as slimes in subsequent beneficiation attempts.

A 2-L stainless steel pressure reactor was used for caustic leaching at elevated temperatures and pressures. This method resulted in the highest degree of liberation. Caustic leaching dissolved the silica binder leaving the surfaces of the zircon grains clean. Figure 3*B* is a photograph of minus 200-mesh zircon grains showing the absence of silica binder adherence.

Table 1 shows the results of each method of liberation when applied to sample A. The crushed minus 20-mesh samples were ground to pass 65 mesh when conventional or attrition grinding liberation methods were investigated. Minus 20-mesh material was used for caustic leaching. Degree of liberation was determined by sizing at 400 mesh and sink-float separating at a specific gravity of 3.3 to isolate the liberated zircon. Rod mill grinding resulted in the lowest grade and recovery of any of the methods. The sink product contained 51.6 pct zircon with a recovery of 48.1 pct of the zircon in the sample. Loss of zircon to the minus 400-mesh slimes was 13.3 pct. Attrition grinding for 10 min resulted in a sink product grade of 83.8 pct zircon with a recovery of 61.5 pct. Loss of zircon to the slimes was 26.4 pct. Attrition grinding for 20 min produced an excessive loss of zircon to the slimes with 41.1 pct reporting to this fraction. Sink product grade was 82.8 pct with a recovery of only 47.6 pct. Caustic leaching with 300 lb/ton NaOH at 160° C for 1 h was the most successful liberation method. The sink product contained 86.0 pct zircon with a recovery of 71.3 pct. A minimal loss of 20.3 pct zircon reported to the slimes.

TABLE 1. - Test results for sample A using four liberation methods, percent

Liberation method	Sink[1]		Float[1]		Minus 400-mesh slimes	
	Grade	Recovery	Grade	Recovery	Grade	Recovery
Rod mill.............	51.6	48.1	8.4	38.6	12.8	13.3
Attrition grind, min:						
10.................	83.8	61.5	8.0	12.1	7.1	26.4
20.................	82.8	47.6	8.8	11.3	6.4	41.1
Caustic leach........	86.0	71.3	3.9	8.4	9.8	20.3

[1]Specific gravity = 3.3.

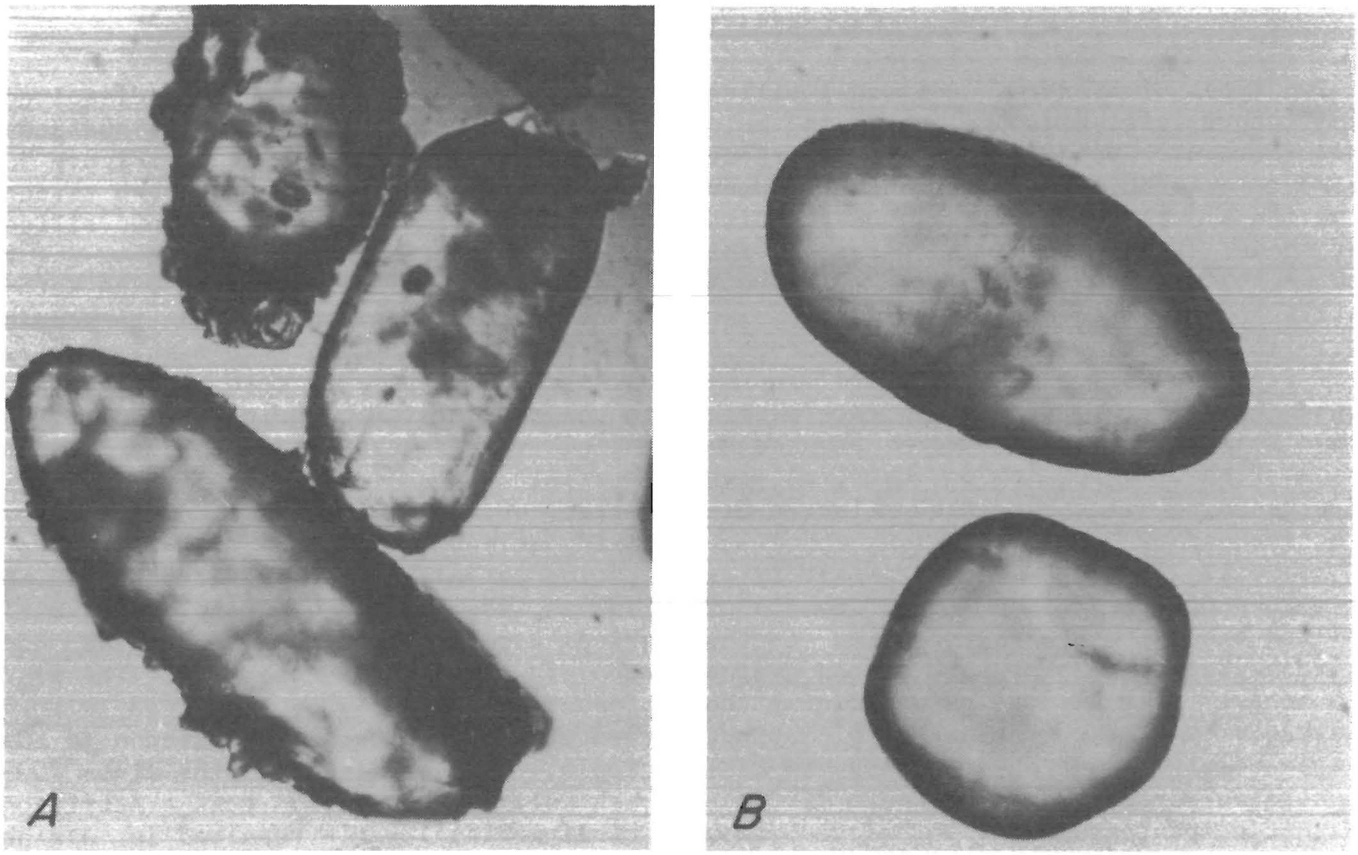

FIGURE 3. - Photomicrograph of zircon particles following (*A*) rod-mill grinding and (*B*) caustic leaching.

BENEFICIATION STUDIES

FROTH FLOTATION

Froth flotation was explored as a means of recovering the zircon in the molds. To develop a successful scheme for use on the waste molds, synthetic mixtures approximating the composition of sample A were prepared and preliminary tests were performed. Various fatty acids, petroleum sulfonates, and amines were investigated as possible zircon collectors. Cocoamine acetate proved to be the most successful collector when used at the rate of 1.0 lb/ton at a pH of approximately 2.5. Investigations of solids content and conditioning time revealed 40 pct solids and 2 min to give optimum results. Two to three cleaner stages were required to produce a clean concentrate. Application of the aforementioned reagents and conditions on a synthetic mixture containing approximately 32 pct zircon resulted in a concentrate containing 90.4 pct zircon with a recovery of 94.3 pct. Table 2 gives the material balance for this test.

TABLE 2. - Flotation of synthetic mold sample

Product	Wt pct	Zircon, pct	
		Assay	Distribution
Concentrate......	34.1	90.4	94.3
Tailings:			
Cleaner 1......	18.1	2.8	1.6
Cleaner 2......	11.8	6.4	2.3
Rougher........	36.0	1.6	1.8
Composite...	100.0	32.6	100.0

Sodium hydroxide exhibited an extreme depressing effect on zircon flotation; therefore, caustic leaching was unsatisfactory as a method of liberation prior to flotation. Sample A was prepared for batch flotation tests by grinding to 65 mesh using a rod mill. Studies on the minimum zircon particle size that would respond to flotation determined 20 µm to be the lower size limit; therefore, all samples were deslimed at this size. Application of the cocoamine acetate flotation scheme resulted in a concentrate containing 69.6 pct zircon with a recovery of 61.2 pct. Table 3 gives the material balance for this test. Caustic leaching and magnetic separation raised the grade of the concentrate to 74.2 pct zircon with an overall recovery of 53.4 pct.

TABLE 3. - Flotation of sample A

Product	Wt pct	Zircon, pct	
		Assay	Distribution
Concentrate......	16.5	69.6	61.2
Tailings:			
Cleaner 1......	9.6	9.8	5.1
Cleaner 2......	3.2	13.2	2.3
Cleaner 3......	3.3	12.8	2.3
Rougher........	44.4	4.8	11.4
Slimes...........	23.0	14.4	17.7
Composite...	100.0	18.6	100.0

GRAVITY CONCENTRATION

A mineral table was used for gravity concentration of the zircon contained in sample A. Zircon with a specific gravity of 4.7 is much heavier than the other constituents in the molds and if liberated a clean concentrate can be made. Samples for tabling tests were ground to pass 65 mesh using a conventional rod mill, then sized at 100, 150, 200, and 400 mesh. Minus 400-mesh material was discarded as slimes. Each size fraction was tabled individually. Table 4 presents the results of one such tabling test. Zircon grade in the composite concentrate was 86.7 pct with a recovery of 61.2 pct. To further upgrade the zircon concentrate, it was then caustic leached for 1 h at 160° C using 300 lb/ton NaOH. This operation raised the grade to 90.8 pct with a zircon recovery loss of less than 1 pct. Chemical and petrographic analysis showed the major contaminant remaining in the concentrate to be iron adhering to the zircon grains. Wet magnetic separation removed more than 87 pct of the iron and raised the zircon grade to 98.6 pct. Zircon recovery in the magnetic separation operation was 93.2 pct. Table 5 shows the material balance for the magnetic separation. Overall recovery for the tabling, leaching, and magnetic separation was 57 pct.

TABLE 4. - Tabling results for sample A

Product	Wt pct	Zircon, pct	
		Assay	Distribution
Concentrate:			
Minus 65 plus 100..	5.0	86.8	25.1
Minus 100 plus 150.	2.6	85.6	13.2
Minus 150 plus 200.	2.8	88.6	14.2
Minus 200 plus 400.	1.8	85.2	8.7
Composite.......	12.2	86.7	61.2
Tailings:			
Minus 65 plus 100..	19.0	12.6	13.8
Minus 100 plus 150.	17.5	3.8	3.8
Minus 150 plus 200.	16.8	4.6	4.5
Minus 200 plus 400.	10.0	4.2	2.4
Composite.......	63.3	6.7	24.5
Minus 400-mesh slimes	24.5	10.1	14.3
Composite.......	100.0	17.3	100.0

TABLE 5. - Magnetic separation results for table concentrate of sample A

Product	Wt pct	Assay, pct		Distribution, pct	
		Zircon	Iron[1]	Zircon	Iron[1]
Magnetic..............	14.2	43.2	17.7	6.8	87.1
Nonmagnetic...........	85.8	98.6	.4	93.2	12.9
Composite..........	100.0	90.8	2.0	100.0	100.0

[1]Total iron reported as Fe_2O_3.

CAUSTIC LEACHING

Caustic leaching studies on samples B and C revealed that high-grade zircon concentrates could be produced by leaching and sizing. All zircon in these samples was minus 325-mesh flour, and sizing at 400 mesh after leaching produced concentrates containing up to 98 pct zircon. Table 6 shows grade and recovery results using various NaOH dosages on samples B and C. All samples were ground to pass 20 mesh with a roll crusher prior to leaching. Each sample was leached at 50 pct solids and 160° C for 1 h. As caustic dosages were increased, recovery also increased while grade remained relatively constant. Figure 4 is a graphic representation of the recovery data contained in table 6. Table 7 shows the effect of a constant reagent dosage and varying time. In this series of tests, 100 lb/ton NaOH was used at 160° C for 1, 2, and 3 h. Increasing leach time tended to increase the recovery but lower the grade.

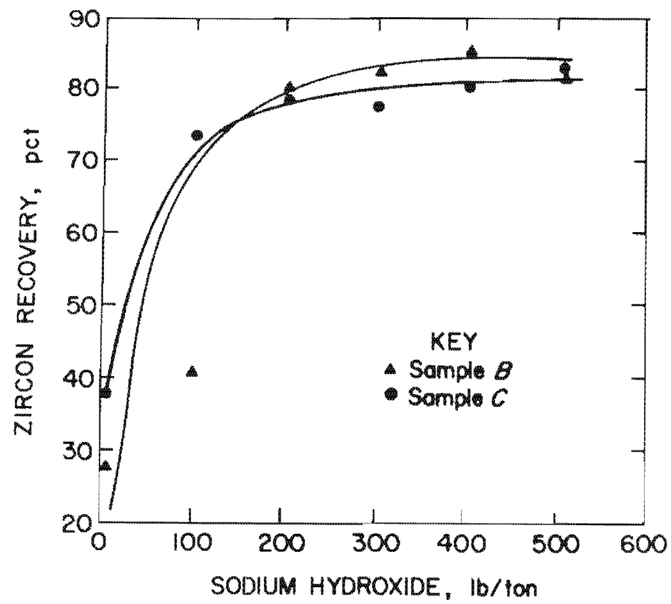

FIGURE 4. - Zircon recovery in minus 400-mesh material as a function of reagent dosage.

TABLE 6. - Effect of NaOH dosage on grade and recovery of zircon in minus 400-mesh material, percent

NaOH, lb/ton	Sample B		Sample C	
	Grade	Recovery	Grade	Recovery
0....	52.1	27.3	59.6	37.9
100....	97.2	41.7	92.6	73.5
200....	98.0	80.8	94.6	78.6
300....	97.8	82.5	95.2	77.4
400....	92.0	85.8	95.4	80.7
500....	82.0	82.3	94.6	82.8

TABLE 7. - Effect of leach time on grade and recovery of zircon in minus 400-mesh material using 100 lb/ton NaOH, percent

Time, h	Sample B		Sample C	
	Grade	Recovery	Grade	Recovery
1......	97.2	41.7	92.6	73.5
2......	93.8	81.2	85.6	79.0
3......	92.8	85.0	85.8	83.9

CONCLUSIONS

Three methods of beneficiation were employed to produce zircon concentrates from waste investment casting molds. Froth flotation followed by caustic leaching and magnetic separation produced concentrates containing up to 74.2 pct zircon with a recovery of 53.4 pct. Gravity concentration by tabling followed by caustic leaching and magnetic separation produced concentrates meeting specification grade from a sample containing coarse zircon. This scheme produced a concentrate containing 98.6 pct zircon with a recovery of 57 pct. Caustic leaching and sizing produced specification grade concentrates from samples containing fine zircon when the other constituents in the molds were coarser grained. Concentrates containing up to 98 pct zircon with a recovery of 81 pct were produced using this method.

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